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D-70548 Stuttgart (DE)**(54) **Method for selectively metallizing a substrate**

(57) A method for selectively metallizing, e.g., for forming an electrical circuit on, a substrate, such as a printed circuit board substrate, a polyimide substrate or a ceramic substrate, is disclosed. Significantly, this method does not involve the use of a photoresist, or of a corresponding chemical developer or photoresist stripper. Rather, in accordance with the method, a layer of seeding solution is formed on a substrate surface of interest. This layer is exposed to light of appropriate wavelength, through a mask, which results in the formation of metal seed on regions of the substrate surface corresponding to the regions of the layer of seeding solution exposed to light. The unexposed regions of the layer of seeding solution are removed by sub-

jecting the exposed and unexposed regions of the layer of seeding solution to an alkaline solution. Thereafter, additional metal is deposited, e.g., plated, onto the metal seed using conventional techniques.

EP 0 687 136 A1

*Cl 1 - photo Rx
don't know phase of
precursor deposit*

Mussy Cal 1-12

heated to 300 degrees C to imidize any polyamic acid which may have formed during the initial base hydrolysis and subsequent immersion in the industrial electroless copper plating bath.

Optical inspection of the polyimide film under a microscope showed that copper had deposited only onto the patterned palladium seeding layer, and nowhere else. The copper adhesion was very good.

Example 4

A thin film of BPDA-PDA was spin coated onto a silicon wafer and heated to drive off the casting solvent and to cure the film to the polyimide structure. This film was base hydrolyzed by immersing the film, for 10 minutes, in the above-described alkaline solution containing sodium hydroxide and N,N,N',N'-tetrakis (2-hydroxypropyl) ethylenediamine. A layer of seeding solution was then formed on the polyimide film by immersing the film, for 30 minutes, in a solution containing potassium trioxalatoferrate and tetraamine palladium chloride.

A patterned palladium seeding layer was formed on the polyimide film by exposing the layer of seeding solution to UV light through a mask. The unexposed regions of the layer of seeding solution were removed by immersing the film in an aqueous, 2M, sodium hydroxide solution maintained at room temperature.

The polyimide film was immersed in an electroless copper plating bath, operated at room temperature, in order to form a strike layer of copper on the patterned palladium seeding layer. Thereafter, the polyimide film was immersed in an industrial electroless copper plating bath in order to deposit additional copper onto the strike layer. Thereafter, the polyimide film was heated to 300 degrees C to imidize any polyamic acid which may have formed during the initial base hydrolysis. The results were the same as those achieved in Example 3.

Claims

1. A method for selectively metallizing a substrate, comprising the steps of:
forming a layer of a solution on a surface of said substrate, said solution having a composition which includes a first metal-containing compound and a photoreactive oxalate compound;
exposing selected regions of said layer to light, to thereby form said first metal on regions of said substrate corresponding to said selected regions of said layer; and
removing said unexposed regions of said layer

from said substrate while depositing essentially no metal onto either said first metal or the unexposed regions of said layer.

2. The method of claim 1, further comprising the step of immersing said substrate in a second metal plating bath, to thereby deposit said second metal onto said first metal.
3. The method of claim 1 or 2, wherein said first metal-containing compound has the general chemical formula ML_mX_n , where M denotes a metal cation, L is a Lewis base ligand and X denotes an anion, and m and n denote integers.
4. The method of claim 3, wherein M is selected from the group consisting of $Pd^{(2+)}$, $Pt^{(2+)}$, $Au^{(+1)}$, $Au^{(3+)}$, and $Ag^{(+1)}$.
5. The method of claim 3, wherein L is a nitrogen-containing ligand, especially NH_3 or ethylenediamine.
6. The method of claim 3, wherein X is selected from the group consisting of $F^{(-1)}$, $Cl^{(-1)}$, $Br^{(-1)}$, $(SO_4)^{(-2)}$ and $(NO_3)^{(-1)}$.
7. The method of claim 1, wherein said photoreactive oxalate compound has the general chemical formula $Y_pM((C_2O_4)_3)_p$ and p denotes an integer.
8. The method of claim 7, wherein Y is an alkali metal ion, especially $K^{(+1)}$ or $Na^{(+1)}$ or $(NH_4)^{(+1)}$.
9. The method of claim 7 or 8, wherein M is $Fe^{(+3)}$ or $Ru^{(+3)}$.
10. The method of any one of the preceding claims, wherein said substrate has a composition which includes epoxy resin.
11. The method of any one of claims 1 to 9, wherein said substrate has a composition which includes a fluoropolymer, said fluoropolymer being polytetrafluoroethylene or a copolymer of tetrafluoroethylene and hexafluoropropylene or a copolymer of tetrafluoroethylene and perfluoroalkoxyvinyl ether.
12. The method of claim 11, wherein said fluoropolymer is an amorphous fluoropolymer and is a copolymer of polytetrafluoroethylene and a compound having a fluorinated dioxole ring segment.

13. The method of any one of claims 1 to 9, wherein said substrate has a composition which includes polyimide, said polyimide including BPDA-PDA, BPDA-ODA or PMDA-ODA.

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14. The method of any one of claims 1 to 9, wherein said substrate is a ceramic substrate, said ceramic substrate including alumina, aluminum nitride and silicon nitride.

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15. The method of claim 2, wherein said second metal is selected from the group consisting from the group Cu, Co, Ni and Au.

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